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Analytical pyrolysis of synthetic chars derived from biomass with potential agronomic application (biochar). Relationships with impacts on microbial carbon dioxide production

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ABSTRACT

A set of 20 biochar samples produced from the pyrolysis of different biomass feedstocks with potential applications as soil amendments were investigated by pyrolysis coupled to gas chromatography–mass spectrometry (Py–GC–MS). The yields of 38 pyrolysis products representative of charred (e.g., benzene derivatives, PAHs, benzofurans) and partially charred biomass (e.g. derivatives of lignin phenols) were evaluated by Py–GC–MS. The estimated yields covered a wide interval (40–7700 $\mu\text{g g}^{-1}$) and were correlated with volatile matter (VM). The proportion of pyrolysis products associated with charred materials ranged from 49 to >99% and was positively correlated with benzene/toluene (B/T) ratios. The molecular distribution of partially charred materials reflected the original feedstock, with higher levels of protein fragments observed in samples with high initial nitrogen content. Both the abiotic and biotic production/consumption of CO₂ was determined in original biochar incubated in water and soil–biochar systems. Large differences were observed in the net CO₂ suppression/stimulation rates, with values between –50 and 2200 $\mu\text{g g}(\text{char})^{-1} \text{d}^{-1}$ for biochar alone and biochar corrected rates from –19 to 690 $\mu\text{g g}(\text{soil})^{-1} \text{d}^{-1}$ for amended soils. In general, increasing pyrolysis temperature yielded biochars with less intense Py–GC–MS pyrolysates, higher B/T ratios, and lower respiration rates. Biochars characterized by higher yields of proteins and cellulose-derived pyrolysis products (e.g. distiller grains, hardwood, mixed wood chips/manure) were associated with higher CO₂ mineralization rates in the corresponding amended soils, particularly sugars. These results suggest that the stimulation in CO₂ production could arrive from the residual non-charred material, and not be a true indication of more completely charred material, which typically had no effect or minimal suppression.

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1. Introduction

Biomass is the only renewable resource capable to substitute oil in both fuel and chemical applications. Among the possible transformation processes, different approaches are based on pyrolysis. By properly selecting operative conditions, pyrolysis can be targeted to the production of gaseous (e.g. gasification), liquid (e.g. flash/fast pyrolysis) and solid (e.g. carbonization) products [1,2], but unavoidably all the three fractions are formed needing a final utilization to sustain the overall process [3]. The solid residue formed upon biomass slow pyrolysis, charcoal, has historical applications dating back to the dawn of human civilization [4]. Charcoal is still used as a solid fuel, a reductant in steel industry, and in the activated form as a sorbent material. However, the production of charcoal from biomass has been proposed as a mechanism to

sequester atmospheric carbon dioxide [5,6]. In addition, potential agronomic and environmental benefits (e.g. reducing soil CO₂, CH₄, and N₂O emissions; adsorption of contaminants, increased soil fertility and crop growth) are receiving increasing interest, with the term biochar capturing both this carbon sequestration benefit and soil fertility improvements [7–9].

The importance of biochar in soil amendment or as carbon sequestration agent and its impact to the environment require a full understanding of its chemical structure and properties [10–14] and the mechanisms controlling its activity in soil [15,16]. The stability in soil is a paradigmatic attribute of biochar when selecting its application in environmental or agricultural applications. Evaluation of volatile matter (VM) in biochar samples was proposed as the simplest method for the evaluation of biochar stability [17]. Other potential indicators have also been proposed, with lower molar oxygen to carbon ratios (O:C) linked with slower laboratory biochar mineralization rates [18]. However, knowledge of the chemical composition of VM is required to rationalize the possible role of the structural properties of biochar and the potential

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role of the VM in observed impacts [19–21]. Py–GC–MS is a reliable method to gather information on the molecular structure of complex organic materials which was applied to the characterization of natural black carbon and charcoal in various geological settings [22–25]. Py–GC–MS was also applied to investigate synthetic black carbon materials [26,27] and possible non-combustion components in black carbon [28]. In the case of natural black carbon, pyrograms above 600 °C were dominated by benzene, toluene, benzonitrile, naphthalene, diphenyl, benzofuran with a similar pattern in the 700–1200 °C interval, therefore this particular set of pyrolysis products was selected as characteristic of black carbon [23]. However, compounds indicative of uncharred material, such as levoglucosan, could be still observed, even at high pyrolysis temperatures [23].

It is interesting to note that the differences in the charcoal composition were minimal between species (e.g., oak, birch, legume) [23], suggesting that the origin of biomass is not a deciding factor for the products of pyrolysis. This conclusion is also supported by the observations of sorbed VOCs on biochar [18,29] suggesting that other factors, such as pyrolysis conditions, post-production processing (e.g., activation), or aging (abiotic oxidation) are the determining factors in terms of organic compound presence and chemical structural arrangement. In fact, relationships were observed between the proportion of black carbon products (e.g., aromatic hydrocarbons and benzofurans) and uncharred/weakly charred biomass (e.g., furans, pyrroles, aldehydes, ketones, alkanes/alkenes), the former products increasing with increasing age from the same system [23], but these relationships are less robust across different pyrolysis facilities [29]. Notably, intensity of observed Py–GC–MS signals may increase with age or oxidation, probably due to partial depolymerisation of the condensed aromatic backbone, even though benzene, toluene and naphthalene maintained their prominence in the pyrolysate indicating an aromatic condensed black carbon fraction [23].

A question may arise to what extent the pattern resulting from Py–GC–MS reflects the original structural features of the char or rather the artificial charring of the analytical procedure. The reliability of Py–GC–MS analysis was supported by comparison with complementary analytical techniques (i.e., NMR, FTIR). Pastorova et al. [30] have found good correlation between qualitative and semi-quantitative data from Py–GC–MS and NMR in the chemical features of char produced from cellulose by slow pyrolysis. Their results, confirmed by FTIR, showed that oligosaccharide units were preserved up to 270 °C when cellulose starts to be degraded into aromatic structures (furans, phenols) forming aromatic chars at 310 °C [30]. The correspondence between the abundance of pyrolysis products indicative of charred and uncharred fraction was supported by a comparison with NMR analysis of natural (fires) charcoal by Kaal and Rumpel [24]. In addition, these authors suggested that the ratio of some alkylated and non-alkylated pyrolysis products could be indicative of charring intensity associated to dealkylation following thermal impact.

Most of the research works on Py–GC–MS were conducted on natural charcoal and black carbon, less investigations were focused to synthetic chars targeted for agricultural soil applications. Moreover, Py–GC–MS studies were typically qualitative. Semiquantitative approach was found useful to find relationships with complementary techniques such as NMR and chemical oxidation [24,30]. However a quantitative approach can be useful to find possible relationships with VM, which is an aspect not yet fully investigated.

In this study a detailed comparison between quantitative Py–GC–MS, physico-chemical analysis and the production of greenhouse gas (CO₂) was accomplished for the first time on a wide set of synthetic biochar samples originating from different feedstocks and pyrolysis conditions.

2. Experimental

2.1. Origin of biochar samples

The various biochars evaluated here were part of ongoing assessments into the impact of biochar additions on greenhouse gas production potentials; research that is part of the USDA-ARS Biochar and Pyrolysis Initiative. The biochar was acquired from various biochar suppliers, entrepreneurs, and research laboratories (see Acknowledgements).

2.2. Ultimate and proximate analysis

Proximal (ASTM D3172) and ultimate analyses (ASTM D3176) were performed by Hazen Research (Golden, CO, USA) and Brunauer–Emmett–Teller (BET) surface area analyses (ASTM D6556) were performed by the USGS (D. Rutherford, Boulder, CO, USA) and Material Synergy (Oxnard, CA, USA). Moisture contents were determined (ASTM D-3173) at 105 °C. Volatile matter was determined as the mass loss from dried sample in covered crucible held at 900 °C for 10 min. Ash was determined as the residual mass left after exposure at 750 °C (uncovered crucible) for 6 h (ASTM D1762). Fixed carbon (FC) was calculated from mass balance (FC = 100–VM–ash).

2.3. Py–GC–MS

Py–GC–MS experiments were performed following a previously described procedure [31]. Shortly, a quartz sample tube containing about 10 mg of exactly weighed biochar sample added with 1 µL of internal standard solution (*o*-isoeugenol at 1000 mg L^{−1} in ethanol) was inserted into the Py–GC interface (300 °C), left a few seconds to evaporate the solvent and then pyrolysed at 900 °C (set temperature) for 60 s by means of an electrically heated platinum filament CDS 1000 pyroprobe interfaced to a Varian 3400 GC equipped with a GC column (HP-5-MS; Agilent Technologies 30 m × 0.25 mm, 0.25 µm) and a mass spectrometer (Saturn 2000 ion trap, Varian Instruments) set at an electron ionization at 70 eV in full scan acquisition (10–450 *m/z*).

Yields were estimated from the ratio of the peak area integrated in the mass chromatogram of a characteristic ion of the selected pyrolysis product and the peak area of the internal standard, the quantity of added internal standard and the amount of sample pyrolysed [31]. An unitary relative response factor was assumed for all the quantified compounds on the basis that our objective was the comparison between samples on a quantitative base rather than the knowledge of the absolute yield of each pyrolysis product. Total yields were the summed yields of all the selected pyrolysis products. A set of 38 pyrolysis products among the most abundant and representative of biological precursors was selected in the calculation of the yields.

Yields were determined at the set pyrolysis temperature of 900 °C as our aim was that to complement VM values (determined at 900 °C) with their molecular composition amenable to GC analysis. Kaal et al. [23] proposed a set temperature of 700 °C as a balance to separate product evolution of pre-existing charred material from that caused by artificial charring during the analysis. At any rate, high pyrolysis temperatures are necessary to obtain informative MS-pyrograms. In fact, detectable pyrolysates from Curie-point Py–GC–MS of highly aromatic chars derived from cellulose could be obtained at 770 °C, but not at 610 °C [30].

2.4. Microbial greenhouse gas production

The agricultural soil was collected at the University of Minnesota's Research and Outreach Station in Rosemount, MN USA

Table 1

Biomass feedstock, pyrolysis temperature and elemental composition of biochar samples. (#: sample identifiers.) Elemental percentages are on a dry mass basis.

#	Feedstock	Pyrolysis temperature (°C)	C	H	N	O	S
S1	Hardwood sawdust	500	63.8	3.03	0.22	11.8	0.01
S2	Hardwood sawdust	500	69.5	3.06	0.32	13.1	0.01
S3	1 year aged S1	500	62.9	2.80	0.32	11.8	0.01
S4	Wood waste	475	81.5	2.42	0.36	7.7	0.01
S5	Wood waste	550	91.4	2.89	0.38	4.6	0.00
S6	Corn stover	815	45.0	1.66	0.50	1.0	0.04
S7	Pine wood chip	465	75.0	3.4	0.30	9.0	0.1
S8	Corn stover	410	25.0	1.1	0.60	5.0	0.04
S9	Pine chip ^a	n/a	43.0	–	2.20	11.0	–
S10	Turkey manure/woodchip	850	1.0	0.5	0.10	3.0	2.1
S11	Pine woodchip	465	71.0	3.3	0.20	11.0	0.1
S12	Corn stover	505	66.0	1.5	1.00	4.0	0.04
S13	Corn stover	515	51.0	0.9	1.00	0.00	0.04
S14	Coconut shell	n/a	87.9	0.06	0.40	<0.01	0.65
S15	Hardwood	n/a	56.9	2.77	0.41	10.5	0.41
S16	Wood chips/manure	n/a	71.1	3.44	0.11	20.6	0.01
S17	Macadamia nut shells	n/a	93.1	2.56	0.67	1.7	0.02
S18	Distillers grain	350	68.6	4.81	7.52	6.6	0.96
S19	Distillers grain	400	69.4	4.31	7.43	5.9	0.90
S20	Wood waste	400	79.8	3.73	0.83	11.9	0.01

^a Mixed with compost after production.

(44°45'N, 93°04'W). Soil at the site is a Waukegan silt loam (fine-silty over skeletal mixed, super active, mesic typic Hapludoll) containing approximately 22% sand, 55% silt, and 23% clay with a pH (1:1 H₂O) of 6.4, 2.6% total organic carbon (TOC), slope <2% and a field capacity moisture content (–33 kPa) of 14.8% (w/w). This site was farmed in a conventionally tilled (moldboard plow) corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.] rotation. The soil was sampled following corn harvest in the fall. Surface soil (0–5 cm) was collected, sieved to <2 mm and homogenized for the incubation study.

Triplicate incubations were established for each biochar (Table 1) with the following combinations of biochar, soil, and deionized water: (1) 0.5 g biochar, (2) 0.5 g biochar + 0.74 mL deionized water, (3) 5 g agricultural soil + 0.74 mL water, and (4) 0.5 g biochar + 5 g agricultural soil + 0.74 mL water. The above incubations were carried out at field capacity (–33 kPa). Incubations were conducted in sterilized 125 ml serum vials (Wheaton Glass, Millville, NJ, USA) and sealed with red butyl rubber septa (Grace, Deerfield, IL, USA). Soil and biochar were manually mixed in the serum bottle prior to moisture additions [8,32]. Biochar control incubations were conducted to assess the production/consumption of CO₂ solely from the biochar with and without water additions (1 and 2). These biochar + water incubations were solely abiotic (no microbial inoculums or soil) and allowed for the correction of the soil + biochar incubations for the impact of the biochar, assuming that the behavior of the biochar was similar in both incubations [8]. The 10% (w/w) amount has been used in previous laboratory assessments [8]. Periodic gas samples were withdrawn from the incubations for analysis on a gas chromatographic–mass spectrometer (GC–MS) system to quantify gas production over a 100-d incubation period, as has been described previously [33]. However, if the O₂ level dropped below 15% during the incubation, the incubation was stopped and the rates of production were calculated up to this point to maintain comparison of aerobic conditions across all incubations.

2.5. Statistics

Results for the CO₂ production activities were arithmetic means of triplicate samples. This rate was determined from the linear increase in headspace CO₂ over the aerobic portion of the production curve. Linear (Pearson) correlation coefficient between two

variables $r(df)$, where df stands for degrees of freedom, was determined for all the investigated parameters. Two set of data were assumed to be correlated when the absolute value of r was larger than the critical value at the level of significance $p = 0.01$ for two-tailed test (Table A in Supplementary materials).

3. Results and discussion

3.1. Biochar properties

Results of biochar characterizations are reported in Tables 1 and 2. The biochars had a range of 1–93% carbon; 1–89% ash; 0.1–7.5% nitrogen; and a range of pyrolysis temperatures from 410 to 850 °C and residence times from seconds to hours (not indicated). This group provides a cross-section of currently available biochars and ashes from biomass utilization. Biochar will be used to describe these materials, even though fundamentally they contain a mixture of black carbon forms spanning ashes, charcoal, char and soot [18].

Surface area (SA, Table 2) encompassed a wide interval of values comparable to literature data for synthetic chars [34]. Although SA tends to increase with increasing pyrolysis temperature and char residence time [11,34] it is not sufficiently indicative of thermal reactivity (e.g. gasification) as it includes SA from micropores which probably do not participate in reactions [35]. Char thermal reactivity is influenced by morphological features (e.g. micro/macropores), in turn determined by the release of volatiles and hence feedstock composition and process conditions, with micropores predominating over macropores in slow pyrolysis [35]. This complex behavior is probably responsible for the absence of marked correspondences with the investigated parameters.

3.2. Py–GC–MS. Total yields

As expected from their different origin, the analysed biochar samples produced different pyrolysate patterns when subjected to Py–GC–MS. Some typical pyrograms are depicted in Fig. 1. Table 2 reports the total yields of pyrolysis products selected for quantitation (Table 3). Not all the identified compounds, some of them exemplified in Fig. 1, were included in the list of Table 3. For instance, levoglucosan, a typical marker of uncharred biomass, was identified in the pyrograms of samples S1 and S15 in Fig. 1, but

Table 2
Surface area (SA, m² g⁻¹), moisture content (H₂O, weight % air dried basis), and proximate analysis of volatile matter (VM), fixed carbon (FC) and ash (weight % on dried weight basis). Yields in μg g⁻¹ and benzene/toluene ratio (B/T) from Py–GC–MS.

#	SA m ² g ⁻¹	H ₂ O % air dry weight	VM % dried weight	FC	Ash	Py yield μg g ⁻¹	B/T
S1	1.0	8.0	28.3	48.9	22.8	3400	1.2
S2	1.0	4.4	30.4	46.0	23.5	3600	1.1
S3	10.0	3.6	25.2	51.9	22.9	2700	1.2
S4	251	8.7	19.3	72.5	8.2	720	2.0
S5	106	1.4	15.5	83.2	1.3	910	1.9
S6	4.4	2.6	30.9	33.2	35.9	1100	1.9
S7	0.1	5.3	36.9	56.5	6.7	2400	1.3
S8	4.2	3.0	41.5	11.9	46.6	2800	1.5
S9	64.0	4.7	26.7	37.1	36.2	6800	0.5
S10	5.0	3.9	7.8	0.7	91.5	41	3.1
S11	0.2	7.2	77.0	10.0	12.9	5800	0.4
S12	17.0	5.3	15.6	44.4	40.0	1300	2.6
S13	10.0	3.7	23.7	21.5	54.8	950	2.6
S14	960	5.5	1.9	84.8	13.3	465	1.8
S15	34.0	6.3	30.3	32.1	37.6	4300	1.0
S16	66.0	3.3	36.4	57.6	6.0	3200	1.3
S17	6.9	9.5	16.8	81.3	1.9	190	0.9
S18	0.3	1.8	44.5	44.6	10.9	7700	0.3
S19	0.3	2.0	37.6	49.7	12.8	6800	0.3
S20	3.5	4.0	26.9	70.2	2.9	4500	1.2

the corresponding GC peak was too broad for a reliable integration. Biochar homogeneity was evaluated by six replicate analyses of sample S1 and resulted in relative standard deviation (RSD) of 23% for total yields. However, repeatability between samples was variable and RSD ranged from 2% (samples S9 and S10) to 85% (sample S14), 30% on average. These results illustrate the chemical heterogeneity that exists even within the same biochar sample.

Yields varied over three orders of magnitude, spanning from 7700 μg g⁻¹ (S18, pyrolysis of distiller grain at 350 °C) down to 40 μg g⁻¹ for the biochar characterized by the highest content of ash (S10). Not surprisingly, a high yield was obtained from sample S9 due to the presence of fresh organic material (compost) added to the charcoal, which is not representative of the biochar itself. Relatively high yields of pyrolysis products were also observed from chars from pine woodchips (S11), distiller grains (S18, S19), and hardwoods (S1–S3) at moderate pyrolysis temperatures (350–500 °C). Biochars S1 and S2 gave very similar yields in accordance to the fact that they were obtained from the same feedstock (hardwood sawdust) under the same operative conditions and pyrolysis unit. Biochar S3 was identical to S1 and S2, but was stored in an open drum for one year (exposed to precipitation and climate) which resulted in a 23% reduction in the corresponding

yield compared to the original material due to the aging and presumed oxidation of some of the sorbed compounds [29].

3.3. Py–GC–MS. Molecular distribution

Pyrolysis products evolved from biochar were grouped into four principal families according to their origin (Table 3): C, charred biomass; H, holocellulose (sugars); L, Lignin; P, proteins. Their individual contribution to total yield is depicted in Fig. 2.

The pyrolysates of all biochar samples were featured by the presence of aromatic hydrocarbons including benzene, benzene derivatives, and polycyclic aromatic hydrocarbons (PAHs; e.g., naphthalene, phenanthrene). Aromatic hydrocarbons (e.g., benzene, toluene, C2-benzenes, naphthalene, phenanthrene, diphenyl) along with benzofurans were grouped into a single family of compounds representing the charred fraction of biochar (C in Table 3). The high proportion of these products in the pyrolysates (% charred) which ranged from 49% (S15) to >99% (S12–S14), indicative of charred biomass. This is in accordance to Kaal et al. [23] who proposed that benzene, toluene, naphthalene, diphenyl and benzofuran could be associated specifically to the charred fraction of black carbon. Similarly, benzene along with naphthalene

Table 3
Pyrolysis products of biochar, the mass to charge ratio (*m/z*) of the quantitation ion and their predominant origin: C, charred biomass; H holocellulose (sugars); L, lignin; P, proteins.

Structural attribution	<i>m/z</i>	origin	Structural attribution	<i>m/z</i>	Origin
Acetic acid	60	H	Guaiacol	109	L
Benzene	78	C	Methyl benzofurans (3 isomers)	132	C
Hydroxyacetone	75	H	4-Ethylphenol	122	L
Pyrrrole	67	P	Naphthalene	128	C
Toluene	91	C	4-Methylguaiacol	138	L
2-Methylthiophene	98	P	Catechol	110	L
Furaldehyde	95	H	4-Vinylphenol	120	L
Ethylbenzene	91	C	5-Hydroxymethyl-2-furaldehyde	97	H
Furfuryl alcohol	98	H	Indole	117	P
<i>m/p</i> -Xylene	91	C	4-Vinylguaiacol	150	L
Styrene	104	C	Syringol	154	L
<i>o</i> -Xylene	91	C	Biphenyl	154	C
2-Cyclopentanedione	98	H	4-Methylsyringol	168	L
Phenol	94	L	<i>trans</i> -Isoeugenol	164	L
Benzofuran	118	C	4-Vinylsyringol	180	L
4-Hydroxy-5,6-dihydro-(2H)-pyranone	114	H	4-Propenylsyringol	194	L
3-Hydroxy-2-methylcyclopentenone	112	H	Phenanthrene	178	C
4-Methylphenol	107	L			

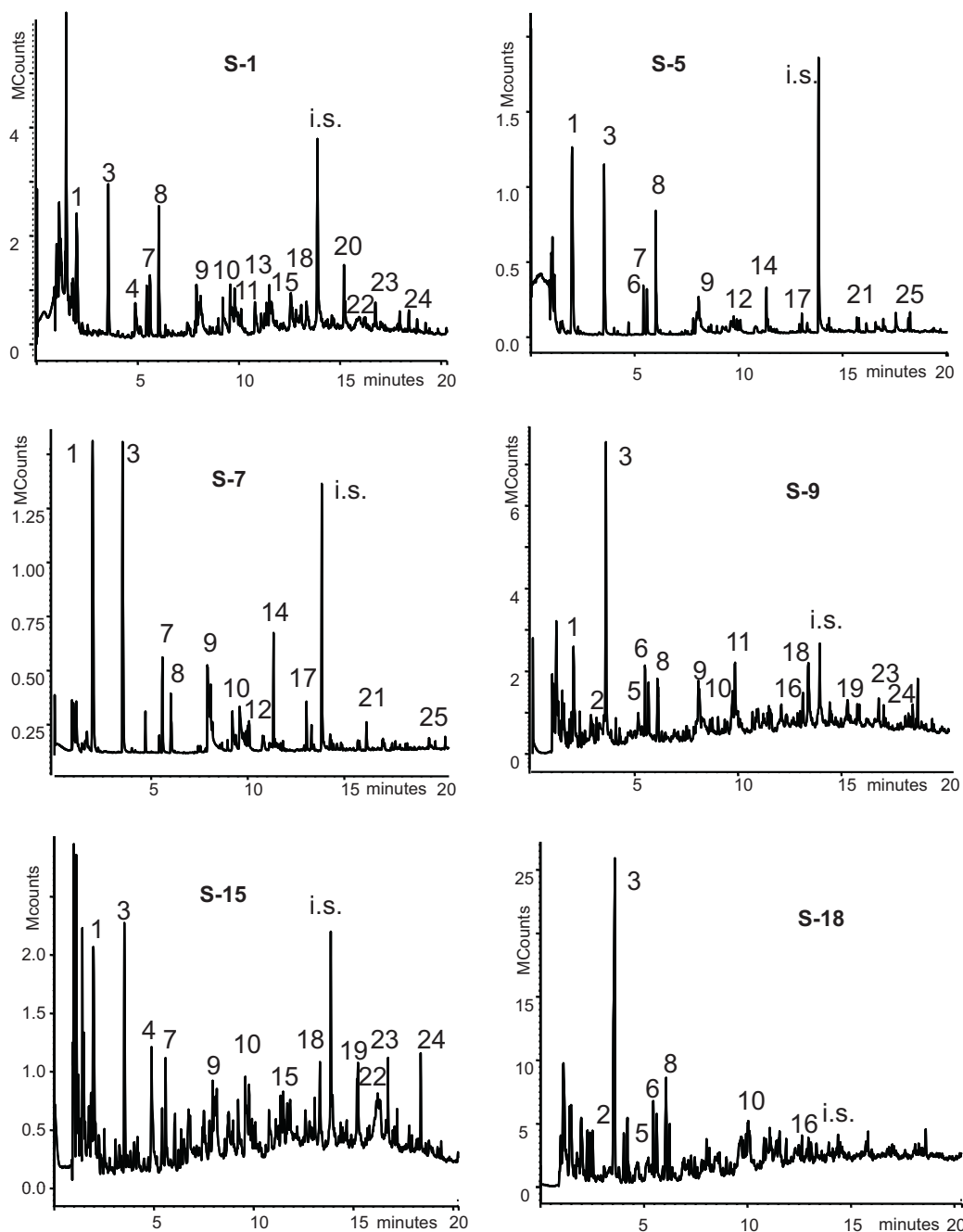


Fig. 1. Total ion chromatograms from Py–GC–MS of biochar S1, S5, S7, S9, S15 and S18 (from top/left to bottom/right). Peak attribution: (1), benzene; (2), pyrrole; (3), toluene; (4), furfuraldehyde; (5), methylpyrrole; (6), ethylbenzene; (7), *m,p*-xylene; (8), styrene; (9), phenol; (10), *p*-cresol; (11), guaiacol; (12), methylbenzofurans; (13), 4-ethylphenol; (14), naphthalene; (15), 4-methylguaiacol; (16), indole; (17), methylnaphthalenes; (18), 4-vinylguaiacol; (19), *trans*-isoeugenol; (20), 4-methylsyringol; (21), dibenzofuran; (22), levoglucosan; (23), 4-vinylsyringol; (24), 4-propenylsyringol; (25), phenanthrene. Internal standard: (i.s.) 5-propenylguaiacol.

and benzofuran derivatives dominated the pyrolysates of cellulose-derived chars with a high degree of aromaticity [30]. The predominance of aromatic hydrocarbons is consistent with the observation that synthetic chars possess high aromatic character (>81%) according to recent ^{13}C NMR studies [11].

In addition, the degree of de-alkylation might be a proxy of thermal alteration [24]. The de-alkylation degree can be estimated in Py–GC–MS from the ratio of parent/alkylated compound, such as benzene/toluene (B/T), ratios. B/T ratios for the biochar pyrolysates ranged between 0.3 and 3 (Table 2) and tended to increase with decreasing overall yields and with increasing the relative abundance of pyrolysis products indicative of charring (% charred). B/T is positively correlated with % charred ($r(18) = +0.64$)

and negatively correlated with the overall yield of evolved products ($r(18) = -0.82$). For example, pyrolysates of biochar samples from corn stover (S8, S12, S13, and S6) were dominated by compounds indicative of charred biomass (% charred >97%) and B/T ratios >1. However, no correlation with pyrolysis temperature (465–815 °C) was observed for these samples. This is not always the case. For instance, biochar S18 and S19 have a rather high % charred with B/T ratios <1. These findings suggest that the B/T ratio is not always a good proxy of charring, and could be related to the fact that the samples were acquired from various pyrolysis units and not the same unit as in other studies [i.e., 24].

Source–structure relationships of pyrolysis products are not always universal. Lignin phenols (phenols, guaiacols and syringols)

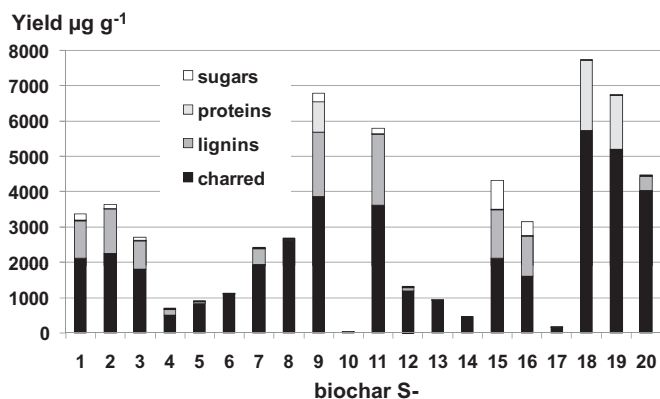


Fig. 2. Yields of pyrolysis products ($\mu\text{g g}^{-1}$) from Py-GC-MS of biochar samples S grouped by chemical families (see Table 3).

represented the second important group of pyrolysis products due to the lignocellulosic origin of the feedstock employed for char production. Pyrolysis products derived from holocellulose (acetic acid, furfuraldehyde and derivatives, cyclopentenones) were also detected (yields of sugars in Fig. 2). These products could be attributed to partially preserved biopolymers which are only weakly charred biomass. They are relatively abundant in biochar from hardwood (S1–S3, S15) and manure (S16), and biochar/compost mixture (S9). However, the distinction of pyrolysis products originated between charred and original biomass is not directly evident in analytical GC-pyrolysis due to possible artifacts of the secondary heating. It is known that the production of aromatic hydrocarbons increases with pyrolysis temperatures between 600 and 800 °C [23]. In this increasing temperature range, lignin phenols decarboxylate, demethoxylate and eventually dehydroxylate, which results with increased production of aromatic hydrocarbons in concomitance with increasing charring, while polysaccharide rearrangements produces furans and probably naphthalenes [30].

Nitrogen-containing compounds may play an important role in the degradability of charcoal as evidenced from the pyrolysis of proteins and are probably less degradable than cellulose [36]. Although nitrogen originally contained in the biomass could be completely lost by volatilization during pyrolysis [37], slow pyrolysis conditions also tend to conserve this element in the biochar [38]. Nitrogen containing compounds indicative of proteins (e.g., indole, pyrrole) and chlorophyll pigments (e.g., pyrrole and alkylated derivatives, these latter identified but not quantified) were detected in most of the pyrolysates. Pyrroles from chlorophyll are rapidly destroyed upon pyrolysis [26]. Thus, proteins might be the main nitrogen source, although inorganic nitrogen sources could also exist. On the other hand, pyrroles might be prone to degradation as these compounds were not observed in the pyrolysates of ancient charcoal [22], although the nitrogen could have been lost during pyrolysis in an open system [37]. In this study, relatively

high yields of indole and pyrrole were evolved from chars S18 and S19 ($\sim 2000 \mu\text{g g}^{-1}$), which correlates to higher elemental nitrogen content (7.5%, Table 1). Interestingly, these chars produced significant levels of 2-methylthiophene, which could be related to the high sulfur levels (Table 1). These chars were obtained from dried distiller grain feedstock, which is the solid residue left after ethanol production from corn grain and may contain sulfur [3]. Similarly, Py-GC-MS of pine wood char mixed with compost (S9) produced significant levels of indole/pyrrole and 2-methylthiophene. Although sulfur is considered a proxy of soot from fossil fuel [27], the occurrence of sulfur-containing compounds in pyrolysates of S18, S19 and S9 indicate that they are also associated with partially charred biomass derived from proteinaceous or N-containing feedstock. Interestingly, indole/pyrrole and methylthiophene were observed in biochar S15 from hardwood.

3.4. Py-GC-MS. Relationships with bulk analysis and CO₂ production

VM is weakly correlated with the yields of pyrolysis products estimated by Py-GC-MS ($r(18)=+0.66$). In general, chars with increased VM tended to produce more intense pyrograms characterized by a lower content of dealkylated (e.g. benzene) aromatic hydrocarbons typical of charred materials. In agreement to this view, % charred is negatively correlated with the O:C ratios ($r(17)=-0.73$). Here, the elemental analysis of the anomalous sample S10 is removed in the calculation of r values. In fact, S10 is the residual of a gasification process, which has combusted a majority of the carbon; the result is a high ash containing residual.

The yield of pyrolysis products associated to proteinaceous materials (pyrrole, indole) is well correlated with the nitrogen content of biochar ($r(17)=+0.97$). This trend is mostly due to the three nitrogen-rich biochar S9, S18 and S19 affording high yields of pyrrole/indole upon Py-GC-MS. A similar correlation was found with methylthiophene indicating that the formation of sulfur-containing compounds might be associated to the presence of proteins (Table 3).

Nitrogen-rich biochar from distiller grains (S18 and S19) yielded pyrolysates with a relatively high level of pyrrole and indole along with aromatic hydrocarbons typical of charred biomass and a low B/T ratio. However, in this case toluene could be derived from the thermal degradation of proteins. These biochar samples exhibited rather high respiration rates, but not the corresponding amended soils. Table 4 shows that net CO₂ production/consumption exhibited large differences for both abiotic biochar samples and biochar-amended soils, in accordance to previous studies [32,39] indicating that the effect of char in soil (priming) is rather variable, with stimulation or suppression (negative values). In general, no clear trends could be revealed between CO₂ production/suppression rates with the chemical characteristics of the chars examined in this study. In particular, VM does not appear to be robust predictor across multiple pyrolysis platforms. Noteworthy,

Table 4
Net CO₂ stimulation/suppression of biochar and biochar amended soils.

#	$\mu\text{g CO}_2 \text{ g}_{\text{char}}^{-1} \text{ d}^{-1}$	$\mu\text{g CO}_2 \text{ g}_{\text{soil}}^{-1} \text{ d}^{-1}$	#	$\mu\text{g CO}_2 \text{ g}_{\text{char}}^{-1} \text{ d}^{-1}$	$\mu\text{g CO}_2 \text{ g}_{\text{soil}}^{-1} \text{ d}^{-1}$
S1	3.4	-13.5	S11	6.4	4.42
S2	2.2	-9.88	S12	4.0	-4.58
S3	4.9	-14.9	S13	2.7	-4.54
S4	15.1	37.9	S14	0.8	-2.00
S5	27.0	30.5	S15	337	649
S6	11.4	-5.39	S16	70.1	21.1
S7	15.4	0.45	S17	2240	-6.54
S8	81.2	0.00	S18	86.4	8.45
S9	511	693	S19	83.6	7.25
S10	-49.6	4.85	S20	149.2	-18.8

the best correlation ($r(18) = +0.73$) was found between the yields of pyrolysis products associated to holocellulose (sugars in Fig. 2) and net production from incubation of biochar-amended soils. However, this correspondence was mainly influenced by biochars S9 and S15 characterized by high respiration rates and a relatively high yield of thermal degradation products from cellulose and relatively low contribution of charred products. Biochars S18 and S19 obtained from distiller grains exhibiting relatively high yields of pyrolysis products from sugars and proteins showed increased respiration rates under wet conditions, suggesting increased C-mineralization. Nonetheless, an increased mineralisation was observed in soil amended with chars S4 and S5, both obtained from pyrolysis of wood waste and characterized by low VM, low yields of pyrolysis products dominated by charred biomass; however, these biochars exhibited the highest surface areas (excluding S14).

When we consider a smaller subset of biochar samples for which pyrolysis temperature of their production was available, weak but significant linear relationships could be observed between pyrolysis temperature and yield of pyrolysis products from Py–GC–MS ($r(14) = -0.66$), B/T ratio ($r(14) = +0.65$) and the net respiration rate of original biochar ($r(14) = -0.65$). Summarizing, biochars (S4, S5, S6, S10 and S12–S14) with a high percentage of charred pyrolysis products (>80%) and high B/T ratios (>1) could be categorised as “high rank” charcoal, with a pyrolytic pattern similar to soot and characterized by the emission of aromatic hydrocarbons as the most important chemical species. These samples are characterized by low O:C ratios (<0.05, S10 is an exception). In general, these biochars are prepared at higher pyrolysis temperatures and tend to give lower biotic/abiotic CO₂ respiration rates, which are indicative of their increased resistance to surface oxidation and microbial mineralization.

Samples S9, S15 and S16 with a lower contribution of charred pyrolysis products (<60%) and smaller B/T ratios, resemble “low rank” black carbons, as they contain a larger amount of oxygenated compounds, phenols and furan derivatives, thus resulting in higher O:C ratios (>0.1). These biochar samples are associated with higher CO₂ respiration rates. These higher CO₂ respiration rates suggest lower resistance to abiotic oxidation and/or microbial mineralization.

4. Conclusions

Pyrolysis–GC–MS of biochar provides a detailed analysis of the molecular composition of VM amenable to GC analysis. The general picture emerging from this study, but with notable exceptions, is that chars characterized by high VM tended to give intense pyrolysates characterized by a significant proportion of thermal degradation products of cellulose and lignin (e.g. biochars from pine woodchip and hardwood) and proteins for those samples rich in nitrogen (e.g. biochars from distiller grains). On the other hand, biochars (e.g. from coconut and macadamia nut shells) with low VM produced weak pyrolysates dominated by aromatic hydrocarbons indicative of charred structures.

The possibility to associate each pyrolysis product with the corresponding precursor, such as cellulose, lignin, protein and charred matter, enabled the elucidation of possible relationships between the occurrence of partially preserved original biomass surviving the carbonization process and the microbial mineralization potential. Increased CO₂ production was observed in soils amended with biochars characterized by a relatively high yield of pyrolysis products associated to cellulose (sugars). The preservation of a thermally less recalcitrant carbohydrate matrix in the biochar did act as a positive priming towards microbial mineralization. However, the absence of universal relationships between respiration rates and chemical characteristics confirmed that the factors governing the

stability of biochar in the environment are highly complex and not easily predictable.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jaap.2011.09.012.

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